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Journal of Polymer Science, Part B

Polymer Letters

Editorial Board: R. M. Fuoss • J. J. Hermans • H. Mark • H. W. Melville • C. G. Overberger • G. Smets

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POLYMER LETTERS VOL. 1, PP. 341-344 (1963)

MEASUREMENT OF A MAXIMUM IN THE ISOTHERMAL CRYSTALLIZATION RATE-TEMPERATURE CURVE FOR POLYPENTENE-1

Several examples of a maximum in the isothermal crystallization rate-temperature curve for polymers have been reported. Takayanagi (1) has observed several in polyesters, and Inoue and Takayanagi (2) one in polyoxymethylene. However, the dilatometric data of Wood and Bekkedahl (3) on natural rubber represent the only literature reference known to the authors on the measurement of a maximum in the overall crystallization kinetics of a polyolefin. The present work presents a second example, that of polypentene-1.

A plot of the reciprocal of one-half the primary isothermal crystallization time versus crystallization temperature (Fig. 1) for polypentene-1 shows a broad maximum centered near 26°C. The polypentene-1 crystallization half-time at the maximum rate is about 3 min.; while natural rubber has a half-time of about 2.5 hr. at the temperature (−25°C.) at which its maximum rate occurs.

The measurements were made on 0.342 g. of sample contained in a volume dilatometer with mercury (28.294 g.) as the confining liquid (4). The total bulb volume was 2.444 cc. at 25°C. The small volume of sample and of mercury enabled thermal equilibrium to be more readily achieved when the dilatometer was transferred from the melting bath (100 or 110°C.) to the crystallization bath preset at the desired tempera-

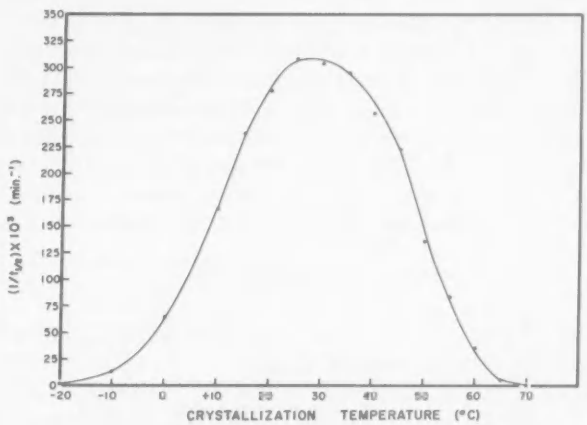

Fig. 1. Reciprocal of the primary crystallization rate half-time vs. isothermal crystallization temperature.

ture. A fast heating rate (0.5 – 1°C. per min.) for the sample from 27°C. up to 80°C. yielded a melting point of 77°C.

The melting bath filled with silicone oil was set at 110°C. for the crystallizations carried out in the temperature range from 35 to 65°C.; boiling water was used to melt the sample for crystallizations carried out in the temperature range from –20 to 30°C. The slopes of the initial portion of the isothermal curve differ depending on what fluid was used in the melting bath as may be seen from a comparison of the curve (Fig. 2) at 40°C. with that at 25°C. These differences may arise from differences in efficiency of heat transfer between the two procedures or from the melting temperature. The mercury level reached the liquidus line (as measured by preliminary melting experiments) in a few minutes, when the sample dilatometer was placed in the melting baths for ten minutes. This indicated that the sample had melted. However, some vestiges of crystallinity may have remained as a result of this melting regime. Isothermal crystallization rates obtained with a dilatometer containing a larger sample (0.673 g.) of mercury were too rapid in the temperature region of maximum rates for delineation of the inflection in the initial portion of the curve to be made. Also, self-heating (from the heat of crystallization) is reduced by using a smaller weight of sample. The crystallization bath (for the temperature range 45–70°C.) contained two

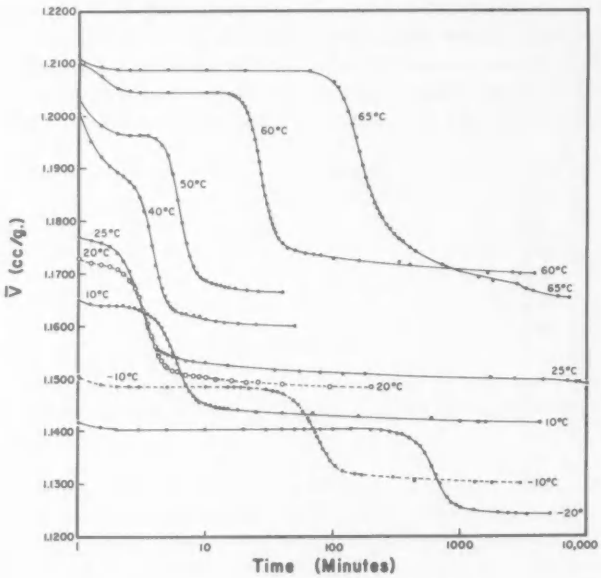

Fig. 2. Specific volume vs. time of isothermal crystallization at different temperatures.

gallons of silicone oil (Dow-Corning 710) and was controlled to within an estimated ±0.05°C. by a thyratron relay thermoregulator circuit. Below 45°C., a crystallization bath containing an ethylene glycol-water solution was used.

The samples were furnished by the Phillips Petroleum Company (Pentene-1, 11272-38-2) and were vacuum-molded to a size convenient for insertion in the dilatometer.

Some typical data on isothermal crystallization rates are shown in Figure 2. Room temperatures (25°C.) was the reference temperature for the specific volume calculations. The estimated change in sample crystallinity on undergoing the transformation from the melt to the maximum amount crystallized at 25°C. is 20%. This estimate assumed the amorphous density value to be 0.85 g./cc. (in agreement with values of amorphous density for the homologous polyolefins polyethylene (0.852), polypropylene (0.85), and polybutene-1 (0.866)) as determined by the liquidus line at 25.0°C., and the unit cell crystal density to be 0.96 g./cc. (5). The low level of crystallinity is in good agreement with the 20% crystallinity found by Wood and Bekkedahl for their maximally crystallized, unstrained natural rubber samples.

The ratio of the temperature at which the maximum rate occurs to the melting temperature shows a value ranging between 0.8 and 0.9 for most polymers measured (6). The ratio has a value of 0.86 in the case of polypentene-1, which is larger than the value (0.82) found for natural rubber. However, other melting point determinations for polypentene-1 carried out by us with slower heating rates indicate that the equilibrium melting point for this polymer is probably greater than 95°C. An increase in T_m of such a magnitude would reduce the value of T_c/T_m to 0.81; a value in good agreement with that for natural rubber. Thus, part of the observed discrepancy probably arises from the lack of attainment of equilibrium melting when heating the imperfectly annealed sample too rapidly.

The slower isothermal crystallization rates for both natural rubber and polypentene-1 compared to those of other polyhydrocarbons (polyethylene, polypropylene, and polybutene-1) probably originates partially from the difficulty in packing awkwardly shaped chains. This difficulty could arise from the bulky pendant side chain in polypentene-1 and from distortion of the main chain in the case of natural rubber (7).

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RELAXATION TIMES IN MOLTEN POLYTETRAFLUOROETHYLENE

Recently, Tobolsky and co-workers (1), found that the maximum relaxation times in molten polytetrafluoroethylene at 380°C. vary as the 0.8 power of the nominal number-average molecular weight. This is in sharp contrast with polystyrene, polyisobutylene, and polyvinyl acetate which have a dependence of maximum relaxation time with the 3.4 power of the number-average molecular weight. The authors suggested as possible explanations a difference in flow properties of the polymers or shortcomings in the molecular-weight determinations based on specific gravity measurements. I would like to advance as a more satisfactory explanation the dissociation of the polymer molecules.

As previously pointed out (2), polytetrafluoroethylene molecules begin a reversible dissociation into free-radical-terminated chain segments at about 365°C. Thus, at 380°C. the polymer chains have substantially dissociated into shorter segments. The longer chains necessarily dissociate into more fragments than do the shorter chains, but at 380°C. the scission process has not been carried to such an extent that the length of the chain segments in the melt is independent of the original molecular weight of the polymer. If the assumption be made that the maximum relaxation time in PTFE is proportional to the 3.4 power of the molecular weight of the radical-terminated chain segments, then the average molecular weight of these segments can be readily calculated to be proportional to the 0.23 power of the number-average molecular weight of the original polymer. This exponent presumably is a strong function of temperature.

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POLYMER LETTERS VOL. 1, PP. 347-349 (1963)

POLYMERS OF DIMETHYL FULVENE

Introduction

There have been only a few reports of the polymerization of the fulvenes, and these are somewhat contradictory. Polymerization has been reported due to heat and pressure (1), to peroxide initiators (2, 3), strong acids and metal chlorides (4), and trichloroacetic acid (5-7). Yet dimethylfulvene is also reported as a good free radical trap (8), and production of gummy materials in presence of metal chlorides has been noted (9). The trichloroacetic acid polymerized fulvene gave a polymer which is under certain conditions electrically conducting.

The purpose of this paper is to report the result of some exploratory work on the polymerization of fulvenes with metal halides, and to give a brief description of the polymers formed.

Experimental

A saturated chloroform solution of the metal halide was added in various amounts to a dilute chloroform solution of the fulvene and allowed to stand for one hour protected from the air in polymerization bottles. The only product studied was the white polymer which precipitated from the solution on the addition of alcohol to the reaction mixture.

Attempts at bulk polymerization, by adding initiator directly to the liquid fulvene gave a viscous liquid or brown gum. The addition of a solution of the metal halide to the pure liquid fulvene gave yellow powders which were difficult to recover and study.

Molecular weights were estimated by cryoscopic methods using benzene as the solvent. Degree of unsaturation of the polymer was estimated by adding dilute bromine solution to a weighed solution of the polymer, followed by the usual iodometric titration. Elementary analyses of the oxygenated products were performed by a commercial service.

Results and Discussion

Dimethyl fulvene gave a chalky white polymer in yields of about 50% using stannic chloride pentahydrate or anhydrous antimony trichloride as initiators. Ferric chloride yielded about 10% polymer, and smaller yields resulted from the use of anhydrous aluminum chloride or anhydrous zinc chloride. The dry white polymer has the notable property of absorbing oxygen from the air rather rapidly, gaining 21.6% by weight in a few hours. The oxygenated product has the average composition $C_8H_{10}O_2$,

which is two oxygen atoms per monomer unit.

Molecular weights in various polymerizations are in the range of 1000 to 5000. The polymer swells and then dissolves readily in hydrocarbon and chlorinated solvents, but not as well in oxygen containing solvents such as acetone or ether. The solution is slightly yellowish in cast. The polymers all had a trace (less than 1%) of chlorine, which may be due to included initiator. On dry distillation the polymer yields about half the initial monomer, with the residue a brown gum. On heating, the polymer begins to darken at about 140°C., but has not melted or softened by 300°C. Reaction with bromine showed about 0.93 double bonds per monomer unit.

The white polymer dissolved in n-hexane has an absorption peak at 243 μ. On addition of trichloroacetic acid, anhydrous antimonic chloride, or hydrochloric acid, the polymer in chloroform or benzene solutions was converted into highly colored species; addition of alcohol destroyed these colors. The highly colored substances obtained are probably due to proton transfer to the polymer; the ability of a polymer to accept protons is taken as evidence that there are conjugated double bonds in the polymer chain.

When the polymer stands in air for a few hours it turns tan in color and becomes virtually insoluble in a wide range of organic solvents, including acetone, benzene, carbon tetrachloride, dimethyl sulfoxide, N, N-dimethylacetamide, and cyclohexane. It is presumed to be an oxygen crosslinked polymer of rather high molecular weight. It does not melt below 300°C. X-ray diffraction shows it to be amorphous. Solutions of the original white polymer open to the air gradually yield a precipitate of the tan oxygenated polymer.

The tan polymer did not yield any yellow oil on dry distillation, nor did a carbon tetrachloride extract of the degradation products give evidence of the presence of fulvenic materials, which are generally characterized by a strong absorption band at 1650 $cm.^{-1}$ (10,11).

While the 6-methyl,6-ethyl fulvene also yielded a polymer, a number of other 6,6-disubstituted fulvenes did not give a polymer under the conditions used, but all gave brightly colored materials and generated heat when their solutions were treated with solutions of metal chlorides.

Polymerization of dimethylfulvene with trichloroacetic acid yielded a tan polymer of about 5,500 molecular weight. A benzene solution of the polymer standing in air became insoluble with no change in color.

Generous financial support of the Central Ohio Section of the Society of Plastics Engineers to H.M. is gratefully acknowledged.

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POLYMER LETTERS VOL. 1, PP. 351-353 (1963)

INVERSION OF A POLYMER AGGREGATE PHASE IN SOLUTION

The copolymer, styrene-maleic acid (SYMA), has an unbranched carbon backbone to which are attached regularly alternating hydrophilic carboxyl groups and hydrophobic phenyl groups (1). The interaction of the carboxyl groups with each other and with the solvent is quite dependent on the degree of ionization of the polyelectrolyte (2). In aqueous solutions of low ionic strength one can expect strong electrostatic repulsion between ionized carboxyl groups. These forces would be manifested in two ways: (a) an extension or uncoiling of the copolymer molecule, and (b) repulsion of neighboring molecules. Interactions among phenyl groups, whether on the same chain or on neighboring molecules, become pronounced in solvents of high dielectric constant (2,3) and might be considered examples of "hydrophobic bonding" (4). Attractive forces among groups attached to a particular molecule would tend to contract the coil and, in the absence of compensating forces, would ultimately cause precipitation. In order for the molecule to exist in solution as a random coil it would seem reasonable to suppose that the solvent must be equally compatible with phenyl and with carboxyl groups. sec-Butanol apparently satisfies this condition since it has the properties characteristic of a θ-solvent (5).

It is possible, by repression of ionization, to prepare aqueous SYMA solutions which have an intrinsic viscosity lower than that for SYMA in a θ-solvent (5). Under these conditions the random coil model fails. Let us suppose that such an anomolous viscosity results from aggregate formation as a consequence of "hydrophobic bonding" between phenyl groups of the copolymer. One then might ask whether or not a solvent could be found such that the aggregate structure could be inverted, i.e., a solvent more compatible with phenyl groups and one in which intra and intermolecular hydrogen bonding might occur.

Intrinsic viscosity measurements of SYMA* in the mixed solvent, isopropanol-benzene, suggested the possibility of an aggregate structure inversion (Fig. 1). Pure isopropanol was a slightly better solvent than

*The styrene-maleic acid copolymer was prepared from a sample of styrene-maleic anhydride (Research Serial No. T-1002) supplied by the Monsanto Chemical Company, St. Louis, Mo.. The anhydride was hydrolyzed in deionized water, 24 hr. at 60°C., shell-frozen, and dried in vacuo. All solutions of the hydrolyzed polymer were aged 48 hr. at 40°C. with intermittent agitation. "Ubbelohde" dilution viscometers were selected such that kinetic energy corrections (less than 1%) could be ignored.

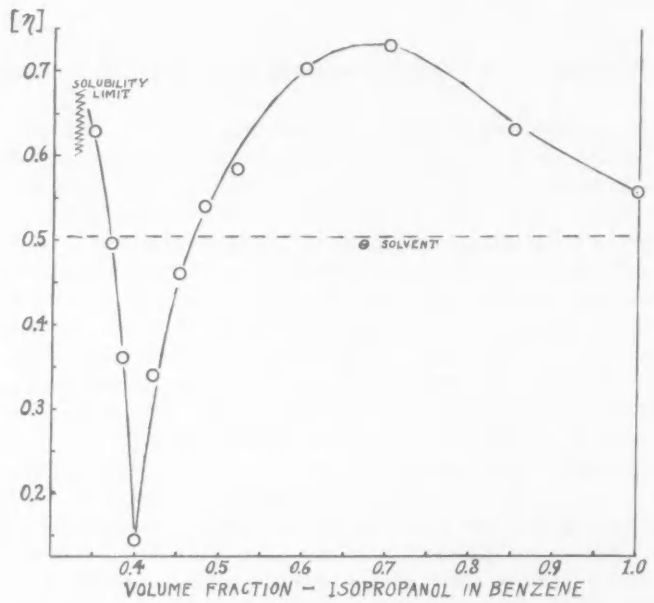

Fig. 1. The intrinsic viscosity $[\eta]$ at 30°C. of styrene-maleic acid copolymer solutions as a function of the volume fraction of isopropanol in the mixed solvent, isopropanol-benzene. The dashed line represents $[\eta]$ of the copolymer in the θ-solvent sec.-butanol (40°C.).

the θ-solvent (sec.-butanol, 40°C.). The solvent power increased with moderate increments of benzene in the mixed solvent and reached a maximum near a volume fraction of 0.7 for isopropanol. Further enrichment of the solvent with benzene decreased the intrinsic viscosity and near a volume fraction of isopropanol equal to 0.4 the intrinsic viscosity fell well below the θ-solvent value, but rose sharply as the volume fraction of isopropanol was still further reduced. Below a volume fraction of 0.33 isopropanol the copolymer was insoluble. Additional evidence for aggregate phase inversion was the observation that coagulation and subsequent slow resolution occurred when the solvent mixture was altered in composition so as to cross the critical volume fraction of 0.4 isopropanol. This effect was shown to be reversible by repetitive crossing of the critical solvent composition.

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POLYMER LETTERS VOL. 1, PP. 355-357 (1963)

A VISCOMETER AND ITS SUPPORT FOR DETERMINATION OF THE INTRINSIC VISCOSITY OF MACROMOLECULAR SOLUTIONS AT ZERO RATE OF SHEAR

The intrinsic viscosity of macromolecular solutions can be closely related to the molecular characteristics of the solute molecules. The value is determined by extrapolating measured values, reduced viscosities, to zero concentration. However the intrinsic viscosity so obtained is "true" only in the case of Newtonian liquids. Many macromolecular solutions behave as non-Newtonian liquids in the range of shear rate. The use of an Ostwald-type capillary viscometer is most commonly accepted for this purpose in scientific laboratories, and the values thus obtained are always "apparent" and depend upon the experimental conditions. The measured values obtained by using the Ostwald viscometer must be extrapolated to zero concentration as well as to zero rate of shear in order to determine the "true" intrinsic viscosity of a given macromolecular solution. A convenient method has previously been reported for the determination of the "true" intrinsic viscosity of non-Newtonian liquids (1). According to the method, the shear rate dependence of the viscosity of a given liquid is measured readily in a single run by tilting the capillary type viscometer. By tilting the viscometer, varying the effective head difference of the liquid, one can change the effective pressure acting on the flowing liquid and thus change the rate of shear. Then the "true" intrinsic viscosity of a given liquid is determined by extrapolating the measured values to zero concentration and zero rate of shear.

In this report a further convenient method for determination of the "true" intrinsic viscosity of macromolecular solutions is given. The principle of this method is the same as the one quoted above, but we

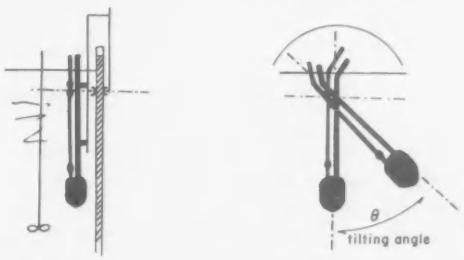

Fig. 1. Schematic diagram of the viscometer and its support.

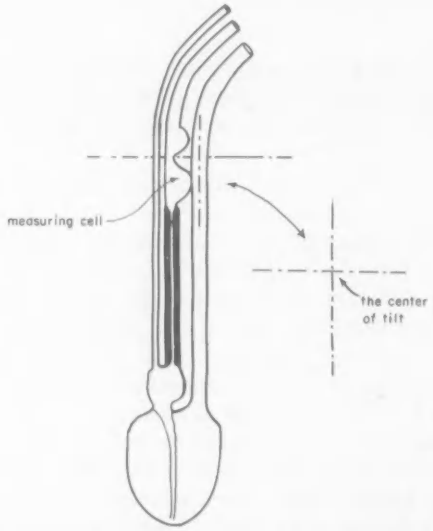

Fig. 2. Modified Ubbelohde-type dilution viscometer.

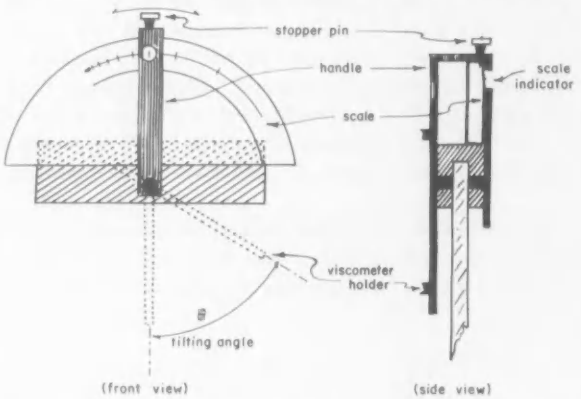

Fig. 3. The constitution and the function of the support.

now use a dilution-type viscometer, a modification of the Ubbelohde viscometer. Schematic diagrams of the viscometer and its support are shown in Figures 1-3.

The "true" intrinsic viscosity of a given macromolecular solution is determined in the following way: (1) Pour the original solution of known concentration of a macromolecule into the viscometer. (2) Affix the viscometer to the support and measure the efflux times at several

fixed positions by tilting the viscometer. By using this support the tilting of the viscometer can easily and instantly be fixed at any desired positions after filling the measuring cell with the solution. (3) After a single run of measurements of the efflux times varying the effective rate of shear, the original solution in the viscometer is diluted with a proper quantity of solvent for the following run. (4) The values of the reduced viscosity thus obtained are extrapolated and the "true" intrinsic viscosity is determined.

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POLYMER LETTERS VOL. 1, PP. 359-363 (1963)

REPRESENTATION OF COMPOSITION AND BLOCKINESS OF THE COPOLYMER BY A TRIANGULAR COORDINATE SYSTEM

Recently Natta et al. (1) calculated a statistical distribution of monomer bonds in a molecule for ethylene-propylene copolymer. It is the purpose of this note to extend the work of Natta and to make an attempt at graphical representation of the relation of copolymer composition with the distribution of bonds between the same and the different monomer units, that is, M_1–M_1 or M_2–M_2, and M_1–M_2, in a binary copolymer molecule. This representation may be generally applicable to any copolymer system, including the block copolymer.

If we designate the fractions of the M_1–M_1, M_2–M_2, and M_1–M_2 bond in a copolymer molecule by X, Y, and Z, respectively, we have

$$X = \theta_1/(\theta_1 + \theta_2 + \theta_3)$$
$$Y = \theta_2/(\theta_1 + \theta_2 + \theta_3) \qquad (1)$$

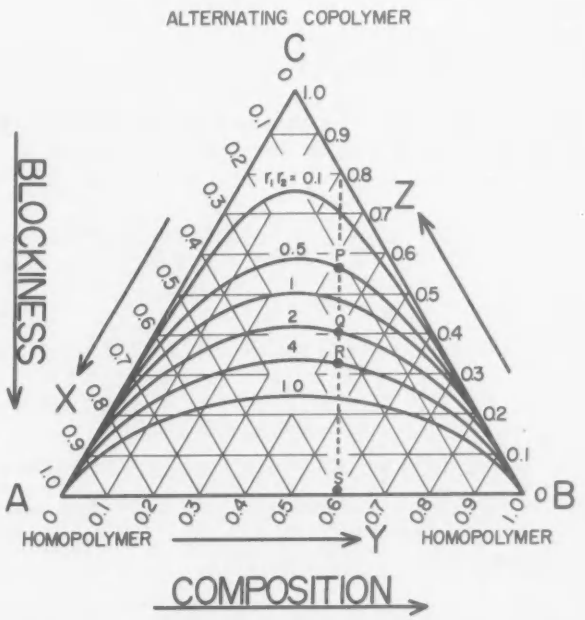

Fig. 1. Representation of composition and blockiness of the copolymer by a triangular coordinate system, according to eq. 13, for various values of the product r_1r_2. The dashed line represents copolymers of the same composition ($1 - \Phi_1 = 0.6$).

and

$$Z = \theta_3/(\theta_1 + \theta_2 + \theta_3)$$

where θ_1, θ_2, and θ_3 are total numbers of the M_1–M_1, M_2–M_2, and M_1–M_2 bond in the copolymer molecule. If X, Y, and Z values are represented by a triangular coordinate system as in Figure 1, each apex of a triangle corresponds to a homopolymer A and B, a perfectly alternating copolymer C. Copolymers, which have the same composition but have different fractions of each bond species, correspond to different points on this coordinate system.

As a special case, for a random copolymer we can calculate these values in the following way. The probability of occurrence of a sequence of the same monomer units M_1 of length n is given by

$$P(n)_{M_1} = P_{11}{}^{n-1}(1 - P_{11}) \tag{2}$$

where P_{11} is the probability for a monomer of the type M_1 to adjoin the other monomer of M_1.

Similarly for M_2

$$P(n)_{M_2} = P_{22}{}^{n-1}(1 - P_{22}) \tag{3}$$

If the total number of blocks composed solely of M_1 or M_2 units are designated by N_1 and N_2, we obtain the following equations:

$$\sum_{n=1}^{\infty} n N_1 P(n)_{M_1} = \Phi_1 N \tag{4}$$

and

$$\sum_{n=1}^{\infty} n N_2 P(n)_{M_2} = (1 - \Phi_1)N \tag{5}$$

where N is the degree of polymerization of a large chain molecule and Φ_1 is the mole fraction of M_1 in the copolymer. From eqs. (2)-(5), we can readily obtain

$$N_1 = (1 - P_{11})\Phi_1 N \tag{4'}$$

and

$$N_2 = (1 - P_{22})(1 - \Phi_1)N \tag{5'}$$

The θ_1 and θ_2 for a random copolymer are calculated as follows:

$$\theta_1 = \sum_{n=2}^{\infty} (n-1)N_1P(n)_{M_1} = N_1P_{11}/(1-P_{11}) \tag{6}$$

and

$$\theta_2 = \sum_{n=2}^{\infty} (n-1)N_2P(n)_{M_2} = N_2P_{22}/(1-P_{22}) \tag{7}$$

which, by substitution of eqs. (4′) and (5′), become

$$\theta_1 = P_{11}\Phi_1 N \tag{6′}$$

and

$$\theta_2 = P_{22}(1-\Phi_1)N \tag{7′}$$

Since $\theta_1 + \theta_2 + \theta_3 = N - 1$, we have

$$\theta_3 = (1-P_{11})\Phi_1 N + (1-P_{22})(1-\Phi_1)N - 1 \tag{8}$$

From eqs. (1), (6′), (7′), and (8) we obtain for large N

$$\begin{aligned} X &= P_{11}\Phi_1 N/(N-1) \simeq P_{11}\Phi_1 \\ Y &= P_{22}(1-\Phi_1)N/(N-1) \simeq P_{22}(1-\Phi_1) \end{aligned} \tag{9}$$

and

$$\begin{aligned} Z &= \{[(1-P_{11})\Phi_1 + (1-P_{22})(1-\Phi_1)]N - 1\}/(N-1) \\ &= (1-P_{11})\Phi_1 + (1-P_{22})(1-\Phi_1) \end{aligned}$$

For an ordinary copolymer, the P_{11} and P_{22} are expressed as follows (2):

$$P_{11} = r_1f_1/(r_1f_1 + 1)$$

and

$$P_{22} = r_2/(r_2 + f_1)$$

where r_1 and r_2 are the monomer reactivity ratios and f_1 is the mole

ratio of M_1 to M_2 in the monomer feed. The relation between Φ_1 and f_1 is given by the following equation:

$$f_1 = \{2\Phi_1 - 1 + [(2\Phi_1 - 1)^2 + 4r_1r_2\Phi_1(1 - \Phi_1)]^{1/2}\}/2r_1(1 - \Phi_1) \quad (10)$$

Using this equation, the above equations can be rewritten as

$$P_{11} = 1 - 2(1 - \Phi_1)/\{1 + [(2\Phi_1 - 1)^2 + 4r_1r_2\Phi_1(1 - \Phi_1)]^{1/2}\} \quad (11)$$

and

$$P_{22} = 1 - 2\Phi_1/\{1 + [(2\Phi_1 - 1)^2 + 4r_1r_2\Phi_1(1 - \Phi_1)]^{1/2}\} \quad (12)$$

Substituting eqs. (11) and (12) into eqs. (9), we have

$$X = \Phi_1 - 2\Phi_1(1 - \Phi_1)/\{1 + [(2\Phi_1 - 1)^2 + 4r_1r_2\Phi_1(1 - \Phi_1)]^{1/2}\}$$
$$Y = (1 - \Phi_1) - 2\Phi_1(1 - \Phi_1)/\{1 + [(2\Phi_1 - 1)^2 + 4r_1r_2\Phi_1(1 - \Phi_1)]^{1/2}\} \quad (13)$$

and

$$Z = 4\Phi_1(1 - \Phi_1)/\{1 + [(2\Phi_1 - 1)^2 + 4r_1r_2\Phi_1(1 - \Phi_1)]^{1/2}\}$$

If the composition Φ_1 and the product of the monomer reactivity ratios r_1r_2 for a binary copolymer system are known, we may calculate the fractions of monomer bonds in a given copolymer using eqs. (13).

In Figure 1, any copolymers of the same composition are represented on the same line vertical to the Y axis. For example, copolymers of the same composition ($1 - \Phi_1 = 0.6$) are represented by points P, Q, and R on the same dotted line. In these copolymers, however, the tendency for making blocks of the same bonds, i.e., blockiness, increases in the order of P, Q, and R. Therefore, by the rectangular coordinate, in which the Y axis is taken as the abscissa and the vertical line to it as the ordinate, the chemical composition and the blockiness of copolymer are represented as shown in Figure 1. Thus, when r_1r_2 is large, Z is small (i.e., blockiness is large), and inversely when r_1r_2 is small, Z is large (i.e., alternation is large) for copolymers of the same composition. In one extreme case, a linear block copolymer with two uninterrupted sequences of each polymeric species ($1 - \Phi_1 = 0.6$) is represented by a point S as shown in Figure 1.

It is concluded from the above considerations that any copolymer may be graphically represented using a triangular coordinate system and the information of the blockiness for the copolymer obtained. Moreover, any copolymer may be characterized with the parameters X, Y, and Z, which were derived in this treatment.

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MELT ELASTICITY IN FRACTIONATED LINEAR POLYETHYLENES

In recent studies involving fractionated linear polyethylenes we have noted marked differences in certain aspects of melt elasticity of the fractionated polymers when compared with whole linear polyethylenes of the same weight-average molecular weight (M_w). This communication is concerned with extrudate swelling and capillary die entry effects in these polyethylene fractions.

1. Extrudate Swelling

Extrudate swelling is well known in both linear and branched polyethylenes (1) and can be attributed in part to an elastic recovery of the deformed entanglement network in the melt. Extrudate swelling increases noticeably with increasing shear stress and the swelling effect is particularly severe in linear polyethylenes, where we have frequently measured extrudate to die diameter ratios in the range 2-4. In fractionated linear polyethylenes however, the extrudate swelling effect may be drastically reduced and in some cases can be totally eliminated. This is shown in Figure 1, in which a swelling index B (defined as the ratio of frozen extrudate to die diameters) is plotted against the log of applied

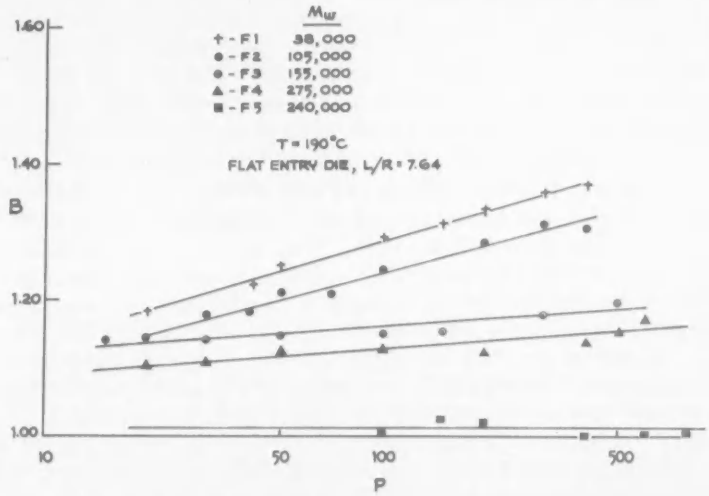

Fig. 1. Swelling index vs. extrusion pressure for fractionated linear polyethylenes with varying molecular weights.

pressure, P, for a number of fractionated linear polyethylene samples. The swelling data refer to extrudates obtained from the C-I-L high shear viscometer (2) operating at 190°C. and fitted with a flat entry capillary with L/R = 7.64 and radius = 0.104 cm. The fractions were prepared by a coacervation method described elsewhere (3). Molecular weights in Figure 1 were obtained from light-scattering data in α-chloronaphthalene solutions at 140°C. Fractions F1-F4 are reasonably sharp with M_w/M_n ratios of about 2, using infrared determinations of terminal unsaturation for estimates of M_n. Sample F5 is a blend of two fractions with respective M_w values of 25,000 and 800,000, prepared by blending the fractions in tetralin solution with subsequent reprecipitation by methanol addition.

The degree of extrudate swelling in Figure 1 is very low in all cases, though there is a tendency for increased swelling at lower M_w. The dependence of swelling on pressure is also unusually low compared with whole linear polyethylenes (see below). In the blended composition F5, no experimentally significant extrudate swelling is detected over the entire range of extrusion pressure investigated. Melt elasticity in all these fractions therefore seems much reduced.

2. Die Entry Effects

Melt elasticity in polymers can be measured from die entry effects (end corrections) in capillary extrusion (2,4). End correction data can be used to calculate a recoverable shear strain which has been shown to increase linearly with shear stress at the capillary wall for some polyethylenes (4). For whole linear polymers this recoverable shear attains a value in the range 5-8 units prior to melt fracture of the polymer. From the slope of the recoverable shear strain vs shear stress plot a shear modulus is found from which a molecular weight can be computed. Theoretically, this molecular weight refers to the molecular weight between entanglement couplings. Experimentally, the molecular weight calculated from the shear modulus has been shown to be in reasonable agreement with light scattering evaluations of molecular weight for a number of linear polyethylenes (4,5). Thus, the molecular weight calculated from the (end correction) shear modulus cannot refer to entanglements of the Bueche-type (6), for which a constant molecular weight between entanglements of the order of 5,000 would be expected for all linear polyethylenes (5). We are apparently dealing with long range molecular couplings of the type noted by Ferry et al. (7), and Gill and Toggenburger (8). The apparent agreement between calculated molecular weights and light scattering determinations noted earlier (4,5) raises the interesting question whether light-scattering data are influenced by long range molecular couplings persisting in some polymer solutions.

End corrections were determined for three of the polyethylene fractions

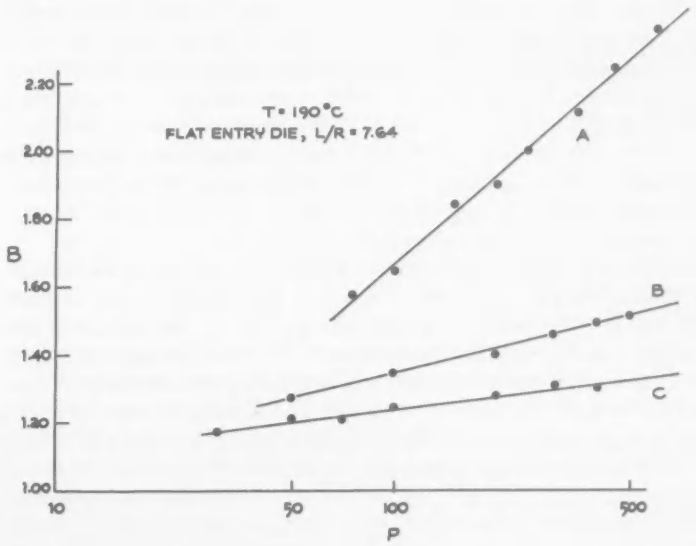

Fig. 2. Comparison of extrudate swelling: (A) whole linear polyethylene (M_w = 100,000); (B) fraction F2 after 1 hr. residence time at 190°C.; (C) fraction F2 (M_w = 105,000).

having M_w values of 78,000, 100,000, and 140,000. In each case the end correction was small and constant at 0.8 ± 0.2 over the entire shear stress range investigated ($\sim 1 \times 10^5$ to 2×10^6 dynes/cm.^{2}). This is the expected value for the Couette correction alone (4). In marked contrast with whole linear polyethylenes therefore, the recoverable shear in each of these cases is constant and vanishingly small over the entire shear stress range, suggesting that no entanglements exist. The swelling index in these fractions was also of the order of 1.1 and nearly independent of extrusion pressure.

3. Discussion

The extrudate swelling and end effect results indicate that these fractionated linear polyethylenes cannot store appreciable amounts of elastic energy during capillary extrusion. If the ability of polymer melts to store elastic energy is due to deformable networks created by chain entanglements (6), then it is apparent that in these fractionated linear polyethylenes the entanglements are few in number or, in some cases, (e.g., sample F5) totally absent. A disentanglement of the polymer networks may occur during the fractionation procedure when the

polymer is kept in dilute solution at elevated temperatures for long periods of time. This suggestion is consistent with a number of the experimental findings reported here. Thus, sample F5 which shows no significant elastic properties at all, is also the material with the most severe solution history, having been subjected to an additional solution-precipitation cycle during fraction blending. The apparent increase in extrudate swelling at lower M_w in Figure 1 is also consistent with the disentanglement hypothesis, since re-entanglement during the experimental time needed for the rheological measurements would logically occur more quickly in less viscous melts.

This point is further elaborated in Figure 2 which shows swelling index data for sample F2 (curve C), a whole linear polyethylene with the same M_w as F2 (curve A), and again for the fraction after it had been allowed to remain in the melt viscometer at zero pressure and 190°C. for 1 hr. (curve B). Curves A and C show the very great differences between extrudate swelling in whole and fractionated linear polyethylenes, while curve B implies a partial recovery of melt elasticity in fraction F2 during its dwell time at a temperature well above the melting point. This could be expected from a partial re-establishment of previously disrupted chain entanglements.

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ON THE VISCOSITY OF GLASS-FORMING POLYMERIC LIQUIDS

The viscosity of a simple liquid is generally found to obey the Arrhenius equation (1).

$$\eta = Ae^{W/RT} \tag{1}$$

where A is a constant, W is the activation energy, R is the gas constant, and T is the absolute temperature. On the other hand, more complicated systems, e.g., liquids with internal structure, exhibit marked deviations from the simple exponential dependence predicted above.

In an effort to overcome this difficulty several modifications of eq. (1) have been put forth (2-4). Another variation will now be introduced which for simplicity is based on a two state model.

Let one consider the kinetic elements of a liquid as being distributed between two energy states (with an energy difference E) in thermal equilibrium. (The lower state is taken to be the zero of energy, while the upper state may be degenerate.)

The activation energy W(T) of a mole of elements will then be assumed to be

$$W(T) = W(0) - E_{conf.} \tag{2}$$

where W(0) is the activation energy of the system when all the elements are in the lower state, i.e., T approaches zero and $E_{conf.}$ is the potential energy gained by the system when a fraction f of the particles are in the upper activated state. If W(T) is substituted for W then eq. (1) may be rewritten as

$$R \ln \eta(T)/\eta_g = W(T)/T - W_g/T_g \tag{3}$$

where the subscript g indicates, the quantities are evaluated at the glass temperature.

If one does a Taylor series expansion about T_g and discards the higher order terms, then eq. (3) becomes

$$R \ln \eta(T)\eta_g = [-W_g/T_g + (dW/dT)_g] (T - T_g)/T \tag{4}$$

Since for a two state system both terms in the brackets are functions only of E/T_g, then a plot of $\ln \eta(T)/\eta_g$ vs. T_g/T (or $(T - T_g)/T$) should be approximately collinear (corresponding states principle) for a wide variety of polymeric substances, i.e., if the limitations implicit in

the derivation of eq. (4) are not exceeded, cf., ref. (5).

It is acknowledged that part of this work was conceived while the author was on a postdoctorate fellowship at Brown University with Prof. J. H. Gibbs.

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CONTRIBUTION TO THE INVESTIGATION OF POLYETHYLENE BY INFRARED TECHNIQUES

Cross and Smith (1,2) have published some works on the detection by an infrared technique of the content of unsaturated groups in various kinds of polyethylene, but without describing, in our opinion, a sufficiently rapid and convenient method.

We have worked on various kinds of commercial polyethylene, obtained through both high and low pressure polymerization, in order to establish some parameters relating to polymerization kinetics. Using the infrared technique we determined, besides the crystallinity, and branching, some values for the terminal and internal unsaturation. These values are at present the object of a further investigation, but we think it could be of interest to make our first results known.

Figure 1 shows the infrared spectra for polyethylene produced by high pressure, Ziegler, and Phillips processes in the region of 1000 to 800 $cm.^{-1}$, where the most suitable bands for the quantitative determination of unsaturation are situated.

Table I gives the positions of the bands and the respective coefficients of molar extinction.

TABLE I

Types of unsaturation	ν, $cm.^{-1}$	ϵ[a]	$12/\epsilon$
RCH = CHR′	964	85.4	0.140
RCH = CH_2	908	121.0	0.099
RR′C = CH_2	888	103.4	0.116

[a]Figures obtained by L. H. Cross, R. B. Richards and H. A. Willis (1).

To calculate the unsaturation expressed in terms of the number of double bonds per 1000 carbon atoms, the following formula is used:

$$[(C=C)/1000\ C] = (12/\epsilon)\ [(1/sd)\ \log\ (A/C)] \qquad (1)$$

where s is the thickness in cm., d is the density at 20°C. in g./cc., and log (A/C) is the optical density measured from the base line. However, as can be seen from Figure 1, the partial overlapping of the vinyl and vinylidene bands make three different methods of graphic resolution necessary, applying the base line and "wings" correction methods.

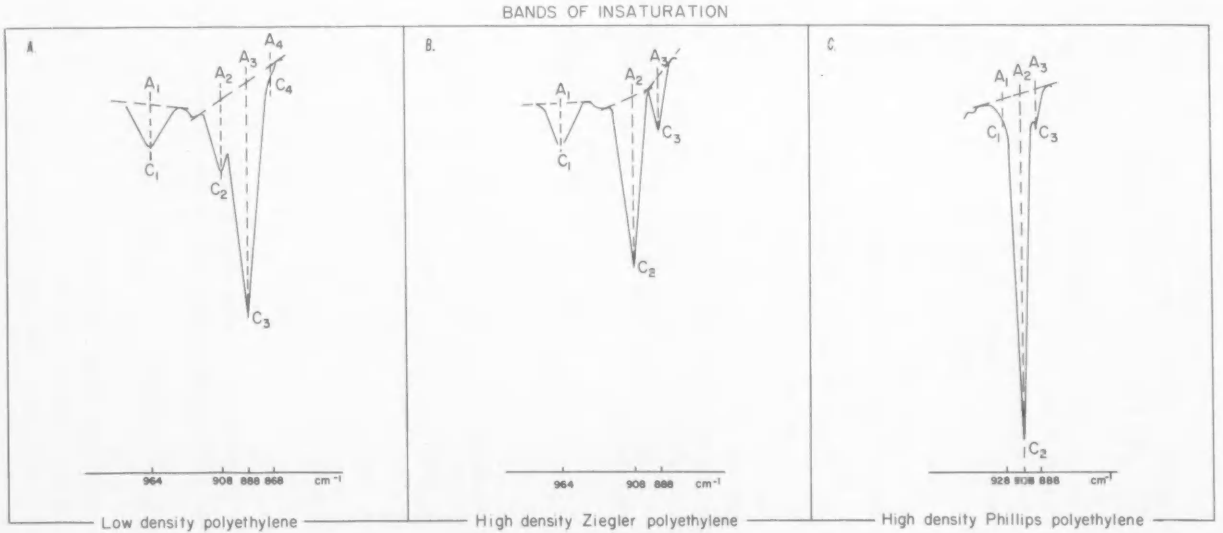
BANDS OF INSATURATION
A
A1
A2
A3
A4
C1
C2
C3
C4
964
908 888 868
cm⁻¹
Low density polyethylene
B.
A1
A2
A3
C1
C2
C3
964
908 888
cm⁻¹
High density Ziegler polyethylene
C.
A1
A2
A3
C1
C3
C2
928 908 888
cm⁻¹
High density Phillips polyethylene

Figure 1.

In the first case (Fig. 1A) the base lines are drawn from about 985 to 945 cm.$^{-1}$ and from about 920 to 860 cm.$^{-1}$. In the second case (Fig. 1B) the base lines are drawn from 985 to 945 cm.$^{-1}$, from 930 to 897 cm.$^{-1}$, and from about 897 to 875 cm.$^{-1}$. In the third case (Fig. 1C) the base line is drawn from about 955 to 875 cm.$^{-1}$. In this polymer the band at 964 cm.$^{-1}$ is not measured, due to its low intensity. It can however be determined by drawing the base line from about 985 to 945 cm.$^{-1}$.

The extinctions are calculated as follows:

$$D_{964} = (1/sd) \log (A/C) \tag{2}$$

$$D_{908} \text{ (1st case)} = (1/sd) [\log (A_2/C_2) - \log (A_4/C_4)]$$

$$\text{(2nd case)} = (1/sd) \log (A_2/C_2) \tag{3}$$

$$\text{(3rd case)} = (1/sd) \log (A_2/C_2)$$

$$D_{888} \text{ (1st case)} = (1/sd) \log (A_3/C_3)$$

$$\text{(2nd case)} = (1/sd) \log (A_3/C_3) \tag{4}$$

$$\text{(3rd case)} = (1/sd) [\log (A_3/C_3) - \log (A_1/C_1)]$$

The content of unsaturated groups is measured by applying the following expressions obtained through the application of eq. (1) for the different types of unsaturation:

$$(RCH = CHR')/1000\ C = 0.140\ D_{964} \tag{5}$$

$$(RCH = CH_2)/1000\ C = 0.099\ D_{908} \tag{6}$$

$$(RR'C = CH_2)/1000\ C = 0.116\ \{D_{888} - [0.95\ (CH_3/1000\ C) + 6.53/29.4]\} \tag{7}$$

The corrective term which appears in eq. (7) was introduced in order to eliminate the contribution of the branching on the band 888 cm.$^{-1}$. It was obtained by using the Bryant and Voter (3), and the Lomonte (4) method, but transforming it to use the values of (CH_3/1000 C) obtained by the compensation method of the polymethylene wedge.

The values of the branching shown in Table II are those obtained by the Willbourn method (5), which has a more general application compared with that of Bryant and Voter (3), the latter being limited to low density polyethylene. The ratio we found for the values obtained with the first and the second methods is 1.16.

TABLE II

Samples[a]	Density 20°C.	Crystallinity %	$\frac{CH_3}{1000\ C}$	$\frac{RCH=CH_2}{1000\ C}$	$\frac{RR'C=CH_2}{1000\ C}$	$\frac{RCH=CHR'}{1000\ C}$	$\frac{RCH=CH_2}{RR'C=CH_2}$
H.d. polyethylene produced by l.p. process (Phillips)	0.9671	76.72	0.54	1.579	0.0299	–	52.81
H.d. polyethylene produced by l.p. process (Standard Oil, Ind.)	0.9577	72.37	6.71	0.240	0.067	2.146	3.582
H.d. polyethylene produced by l.p. process (Ziegler)	0.9548	66.11	3.09	0.430	0.090	1.121	4.778

L.d. polyethylene produced by h.p. process	(a)	0.9257	45.36	17.62	0.045	0.195	0.053	0.231
"	(b)	0.9258	45.77	16.74	0.059	0.219	0.051	0.269
"	(c)	0.9197	42.83	19.49	0.074	0.339	0.078	0.218
"	(d)	0.9190	44.70	23.86	0.083	0.368	0.076	0.226
"	(e)	0.9181	42.81	24.16	0.099	0.416	0.095	0.238
"	(f)	0.9182	43.16	24.42	0.101	0.393	0.101	0.257
"	(g)	0.9181	43.24	25.06	0.096	0.397	0.082	0.242
"	(h)	0.9175	40.29	26.68	0.101	0.492	0.099	0.205
"	(i)	0.9172	40.97	28.05	0.107	0.569	0.122	0.188

[a]H.d. = high density; l.p. = low pressure; L.d. = low density; h.p. = high pressure.

The values of the crystallinity (Table II) were obtained by applying the following relation:

$$\text{Crystallinity } \% = 9.54 + 12.89\ D_{1894} \tag{8}$$

where

$$D_{1894} = (1/s) \log (A/C) \tag{9}$$

with s being the thickness in cm., and log (A/C) the optical density at 1894 $cm.^{-1}$ measured from the base line, drawn from about 1950 to 1850 $cm.^{-1}$. This was obtained through a calibration of the values of the extinction of the band at 1894 $cm.^{-1}$ on the basis of the crystalline content of a series of polyethylene samples whose crystallinity had been obtained experimentally by applying the method and the general equation of Hendus and Schnell (6). The above practice proved simpler and more precise than the previous Tobin and Carrano method (7).

Our procedure has the advantage of being considerably simpler than that of Schnell, because it permits a reliable calculation of crystallinity directly from the measure of extinction at 1894 $cm.^{-1}$ alone. The use of this method becomes necessary in cases where the crystallinity of oxidized, degraded, or in some way modified polyethylenes must be measured. Such polymers in fact give false bands in the region 1500 to 1000 $cm.^{-1}$ which cover, or in any case render useless, the amorphous band at 1303 $cm.^{-1}$.

The values shown in Table II, which refer to studies carried out on various samples of commercial polyethylene, agree quite satisfactorily with those given in the literature quoted.

The data on the content of unsaturated groups is worth a more careful examination. The determination of the quantity of such groups emphasizes the importance of their relative distribution, especially regarding the terminal, vinyl and vinylidene unsaturations, the ratio of which depends upon the process by which the polymer is produced. As can be seen from the last column of Table II, for a polymer obtained by a high pressure process the ratio is about 0.2, for a Ziegler polymer about 4, while for a Phillips product it is higher than 50. These values are very far apart, and the differentiation is therefore distinct.

Although our results are too limited for definite conclusions to be drawn and suggest that other experiments are desirable, they do indicate a distinct differentiation in the type of polyethylene according to the distribution of unsaturated groups.

The test pieces of polyethylene were obtained by compression molding. They were 200 to 300 μ in thickness and their densities were measured at 20°C. by the gradient tube method. Before being measured, the test pieces were conditioned in accordance with the ASTM (D 1248-60T) specifications for polyethylene.

For the infrared studies a Perkin-Elmer spectophotometer 221 grating, with 927 program, and a rate of 40 cm.$^{-1}$/min. was used. To eliminate fringes of interference when the studies were carried out in the presence of air, the test pieces were supported between two plates of NaCl, using a fine layer of Nujol to ensure that they adhered completely to the plates.

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THE INFLUENCE OF pH ON THE POLYMERIZATION OF VP

It had been reported in the literature that ammonium hydroxide enhanced the polymerization of vinyl pyrrolidone (1). In the course of studying the chain transfer reactions of dextran with PVP radicals in aqueous medium (2) in the presence of ammonium hydroxide, a maximum in the rate of polymerization was observed between pH 8.6 and 9.5. In order to distinguish whether the effect of NH_4OH on the rate of polymerization of vinyl pyrrolidone was a specific one, or merely due to pH variation, the following rate studies at different pH values were undertaken.

The pH values of the aqueous solutions (total volume of 50 ml. at 20°C.) which contained 30% n-vinylpyrrolidone, 2.4×10^{-3} mole/liter of azobisisobutyronitrile and dilute ammonium hydroxide or 2 ml. of buffer solutions, were determined by a Model GS Beckman pH meter at room temperature. The solutions were flushed with nitrogen, repeatedly degassed, sealed, and then polymerized at 50°C. ± 0.1°C. with shaking device. The rate of polymerization was determined from the percentage of conversion for each sample at different time intervals. The conversion was below 35% in each case.

The variation in the rates of polymerization of vinyl pyrrolidone with pH is shown in Figure 1. Each set of data from the two different systems fell on the same curve. The rates of polymerization were fairly constant between pH 6 and 7, and began to increase sharply at pH 8.

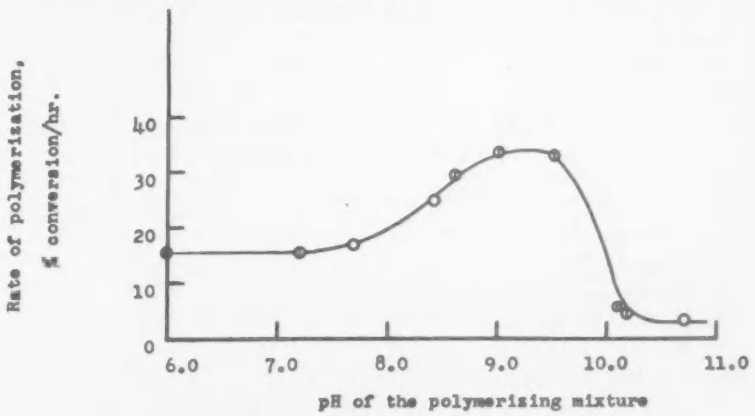

Fig. 1. Effect of pH on the rate of polymerization of VP at 50°C. (VP) = 2.7027 moles/liter; (AZBN) = 2.439×10^{-3} mole/liter; (O), VP + H_2O + ABIN + NH_4OH; (Φ), VP + H_2O + ABIN + buffer solutions; (●), VP + H_2O + ABIN.

The maximum occurred between pH 8.6 and 9.5. Above pH 10, the rate of polymerization became much lower than that of pH 6.0. This pH dependence of the rate of polymerization of VP was not reported previously.

It is interesting to see from Figure 1 that the rate of polymerization of vinyl pyrrolidone is a function of pH alone regardless of the presence or absence of NH_4OH. This would exclude any specific effect of the ammonium hydroxide on the rate of aqueous polymerization of VP, as initiated by azobisisobutyronitrile.

It was reported by Blauer (3) that the rate of polymerization of methacrylic acid initiated by ABIN in aqueous medium varied with pH. Between pH 6 and 12, the rate of polymerization also changed through a small maximum as with vinyl pyrrolidone and decreased at pH 12. The dependence of the rate of polymerization of methacrylic acid on pH in the region pH 6 to 12 is remarkably similar to that found with VP in the present study. Blauer assumed that the rate of initiation by ABIN was constant in aqueous medium and offered the explanation that the change in the rate of polymerization was due to the change in the rate of bimolecular termination of ionized and unionized polymethacrylic acid radicals. In as much as vinyl pyrrolidone is a nonionic monomer, the above explanation is not applicable to our results. It appears that the validity of the assumption of a constant rate of initiation by ABIN in aqueous media at different pH may be questioned. A study of the decomposition of ABIN in a water-dioxane mixture at different pH will be published elsewhere.

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LOW SHEAR VISCOSITY OF POLYPROPYLENE MELTS

Current theories (1) relate the zero shear viscosity to the weight-average molecular weight for polymer melts having narrow molecular weight distributions and to a rheological molecular weight average between $\bar{M}_w$ and $\bar{M}_z$ for disperse polymer distributions. Most published data (2-4) indicate that a straight line logarithmic relation having approximately a 3.5 slope exists between the zero shear melt viscosity and the weight-average molecular weight. The present note describes the results of preliminary studies of the low shear behavior of experimental polypropylene resins in a capillary rheometer.

A series of polypropylene resins ranging in decalin intrinsic viscosity from 1.00 to 3.75 were examined in a nitrogen pressured capillary extrusion rheometer. Zero shear viscosities were estimated by the method

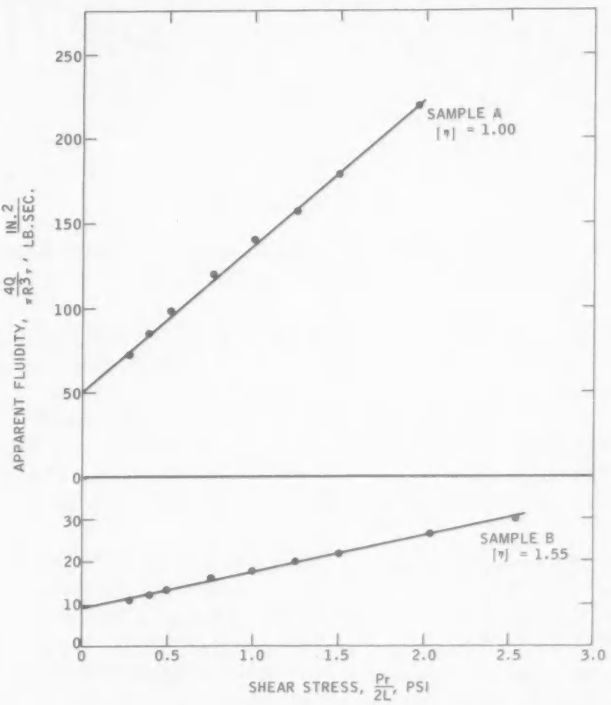

Fig. 1. Apparent fluidity vs. applied shear stress-low molecular weight resins 400°F., 0.0398 × 2.000 in. stainless steel capillary.

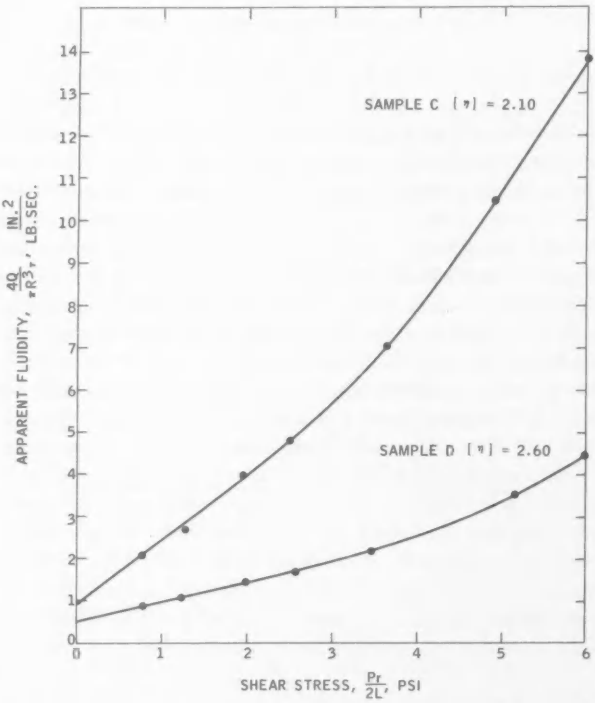

Fig. 2. Apparent fluidity vs. applied shear stress-high molecular weight resins. 400°F., 0.0398 × 2.000 in. stainless steel capillary.

suggested by Schrieber and Bagley (5) in which the apparent fluidity is plotted against the applied shear stress. In general, good straight lines were obtained for resins having intrinsic viscosities of about 1.7 and less. Figure 1 shows typical plots obtained for representative resins of low intrinsic viscosity. With resins of higher intrinsic viscosity, curvature was observed but extrapolation was nevertheless possible. Figure 2 shows typical plots obtained for resins of relatively high intrinsic viscosity.

Extrapolated zero shear viscosities obtained at 400°F. are plotted in Figure 3 as a function of the intrinsic viscosity of the rheometer extrudates, determined in decalin at 135°C. Although some scatter is present, the data are correlated well by a straight line of slope 4.5 ± 0.3. Since the reported relationship (6,7) between intrinsic viscosity and $\bar{M}_v$ has a Mark-Houwink exponent of 0.8, the slope of the line plotted as a function of $\bar{M}_v$ is approximately 3.6 ± 0.2. Furthermore, for this exponent, the $\bar{M}_v/\bar{M}_w$ ratio will remain essentially constant for real disperse

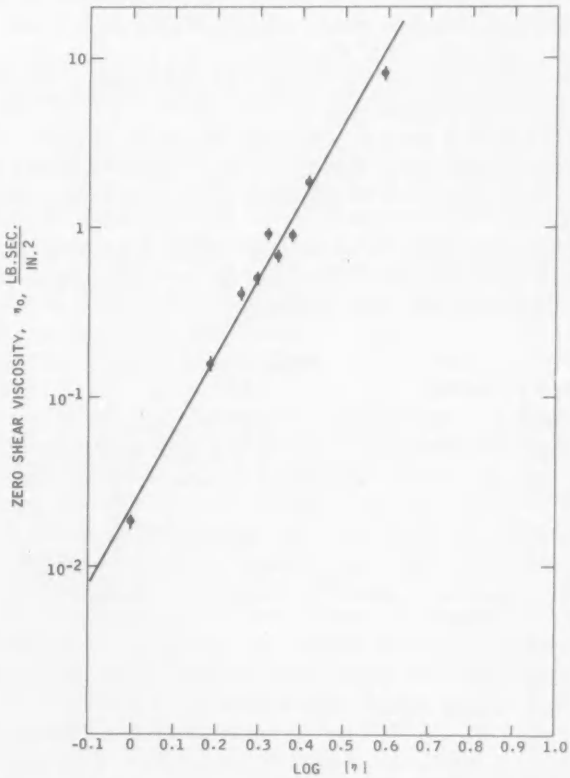

Fig. 3. Zero shear viscosity vs. extrudate intrinsic viscosity. 400°F., 0.0398 × 2.000 in. stainless steel capillary.

distributions. It may, therefore, be concluded that the zero shear viscosities of the polypropylene samples studied should be proportional to the 3.6th power of the weight-average molecular weight. As indicated earlier, Bueche (1) has proposed that the zero shear viscosity is related to a rheological molecular weight intermediate between the weight- and z-averages, and closer to the z-average in the case of disperse distributions. This relationship is given by $\eta_0 = K\bar{M}_t^{3.5}$, where η_0 is the zero shear viscosity, $\bar{M}_t$ is the "rheological molecular weight" and K is a proportionality constant. The experimental data reported here may therefore be interpreted in several ways:

1. Some of the molecular components of the samples studied may not satisfy Bueche's requirement that all species be larger than a critical size. The presence of low ends may therefore mask the predicted effect of high ends. This has been suggested by Fox and Allen (8).

2. Many proposed molecular weight distribution models (e.g., Wesslau's with high molecular weight cut-offs, Schulz-Zimm's, and Tung's) yield relatively constant $\bar{M}_z/\bar{M}_w$ ratios. It is, therefore, indeed possible that a correlation between η_0 and $\bar{M}_z$ could be obtained, if accurate values of $\bar{M}_z$ could be determined.

3. The observed deviations from the line shown in Figure 3 actually may be due in part to variations in $\bar{M}_z/\bar{M}_w$. These variations may very well be larger than would be indicated by the present extrapolation.

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FAR INFRARED SPECTRA AND THEIR VIBRATIONAL ASSIGNMENTS OF ISOTACTIC POLYPROPYLENE

In our previous study (1), the polarized infrared spectra of isotactic polypropylene were measured in the region of 600-280 cm.$^{-1}$. In the present study, the far infrared spectra of isotactic or atactic polypropylene were measured in the region 410-80 cm.$^{-1}$ as shown in Figure 1. A Perkin-Elmer Model 201C Far Infrared Spectrometer was used. Crystalline solid sheets of isotactic polypropylene (of thickness 3 mm.) were prepared by pressing Moplen (Mitsubishi Petrochemical Co. Ltd.) at 190°C. The atactic sample was synthesized at 70°C. in n-heptane solution with $AlCl_3$ as a catalyst. The liquid fraction, not boiling below 290°C., was collected for spectroscopic measurements. As shown in Figure 1, the isotactic sample exhibits sharp bands whereas the atactic sample does not exhibit well-defined absorption bands.

The infrared dichroism was also measured for a uniaxially oriented sheets (of thickness 2 mm.) of isotactic polypropylene. A pair of polyethylene polarizers were used. The observed spectra are shown in Figure 2. The parallel bands at 398, 251, ~200, and 155 cm.$^{-1}$ may be assigned to the A fundamental vibrations whereas the perpendicular bands at 321, ~210, and 169 cm.$^{-1}$ may be assigned to the E($2\pi/3$) vibrations.

In order to elucidate the nature of these bands, the infrared active vibrations were calculated by the general method for treating helical polymers (1,2). In the present study the modified Urey-Bradley potential

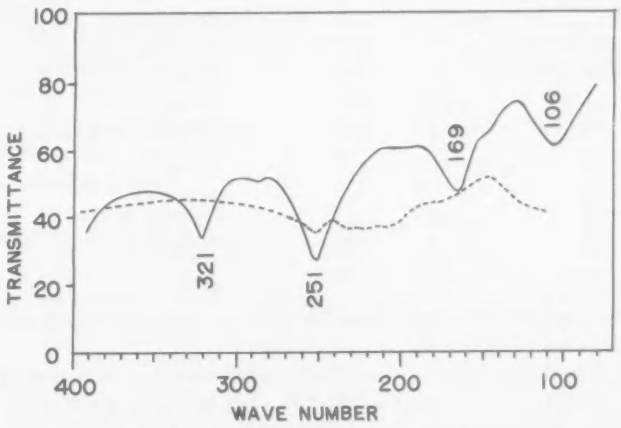

Fig. 1. Far infrared spectra of isotactic (solid curve) and atactic (broken curve) polypropylene.

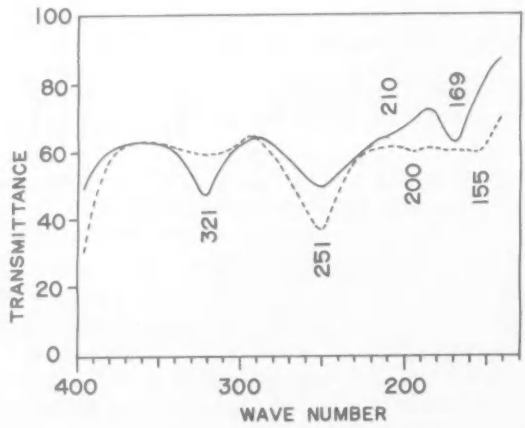

Fig. 2. Polarized far infrared spectra of a uniaxially oriented film of isotactic polypropylene; the solid curve was measured with the electric vector perpendicular and the broken curve with the electric vector parallel to the direction of orientation.

TABLE I

The A and E($2\pi/3$) Frequencies (cm.$^{-1}$) Below 600 cm.$^{-1}$ and Potential Energy Distributions (%) of Isotactic Polypropylene

$\nu_{obs.}$*	$\nu_{calc.}$†		Potential energy distribution‡
528 (⊥)	ν_{21} (E)	491	δ^a (30), δ^s (20), δ (20)
460 (⊥)	ν_{22} (E)	448	δ^s (55), δ^a (15)
456 (∥)	ν_{21} (A)	445	δ^a (75)
398 (∥)	ν_{22} (A)	381	δ^s (45), δ^a (30)
321 (⊥)	ν_{23} (E)	294	δ^a (65)
251 (∥)	ν_{23} (A)	266	δ^a (30), δ^s (25), t_{CM} (20)
~210 (⊥)	ν_{24} (E)	222	t_{CM} (95)
~200 (∥)	ν_{24} (A)	216	t_{CM} (75)
169 (⊥)	ν_{25} (E)	145	δ^a (40), δ (35)
155 (∥)	ν_{25} (A)	138	δ (40), $t_{CC}{}^e$ (30)
106	ν_{26} (E)	70	$t_{CC}{}^a$ (80)

*Observed frequency; ∥: parallel band; ⊥: perpendicular band.

†Calculated frequency.

‡δ^s and δ^a: the symmetric and asymmetric deformation modes of the CH_2–$CH(CH_3)$–CH_2 group; δ: CH–CH_2–CH bending; $t_{CC}{}^a$, $t_{CC}{}^e$, and t_{CM}: the internal rotation modes about the axial C–C bonds, the equatorial C–C bonds, and the C–methyl bonds, respectively.

function as used previously (1) was supplemented with the internal rotation potential about the axial C–C bonds, the equatorial C–C bonds, and the C–methyl bonds (the method for treating internal rotation vibrations will be reported elsewhere). The potential constant of Y = 0.0937 mdyn. · A./rad.^{2} corresponds to the threefold internal rotation potential with the barrier height of 3 kcal./mole.

As shown in Table I, the calculated frequencies (below 600 cm.$^{-1}$) agreed well with the observed frequencies. Therefore, the potential energy distributions were also calculated. The weak parallel band at about 200 cm.$^{-1}$ and the perpendicular band at about 210 cm.$^{-1}$ are due to the internal rotation mode of the methyl group. The internal rotation mode about the equatorial C–C bond is involved in the A vibration at 155 cm.$^{-1}$. The band observed at 106 cm.$^{-1}$ corresponds to the calculated E($2\pi/3$) frequency of 70 cm.$^{-1}$. This is the internal rotation vibration about the axial C–C bond. The frequency deviation may be ascribed partly to the neglect of the interchain potential energy.

The low frequency bands of isotactic polypropylene arise from skeletal bending modes and/or the internal rotation modes. These modes are not localized in a single repeating unit, and accordingly give rise to well-defined bands only for highly ordered helical structure of isotactic polypropylene.

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CIS-OPENING POLYMERIZATION OF PROPYLENE AS REVEALED BY INFRARED ANALYSES OF DIISOTACTIC POLY(PROPYLENE-$1d_1$)

A number of poly(alkyl alkenyl ethers) were synthesized by Natta et al. (1). The x-ray diffraction of fibers of poly(trans-propenyl isobutyl ether) was studied and this polymer was found to be threo-diisotactic (2). Accordingly the polymerization of propenyl alkyl ethers was found to occur by the cis-opening of the double bond. In this connection it is interesting to inquire whether the polymerization of propylene with Ziegler-Natta catalysts occurs also by the cis-opening of the double bonds or by the trans-opening.

Poly(propylene-$1d_1$-cis) [Poly-cis] and poly(propylene-$1d_1$-trans) [Poly-trans] were synthesized (3) and the polarized infrared spectra (4000-600 cm.$^{-1}$) of these polymers were found to be quite different from each other, indicating that the structures (or the positions of the deuterium atoms) of these polymers are different too (4).

In our previous study, a general method for treating the normal vibrations of helical polymers was worked out (5,6) and was applied for calculating the infrared-active A and E($2\pi/3$) vibrations of isotactic polypropylene (6,7). In the present study, the A vibrations of the threo- and erythro-diisotactic poly(propylene-$1d_1$)* were treated since a number of strong parallel bands arising from these A vibrations have been observed for poly-cis and poly-trans (4).† The intramolecular potential function has been reported previously (6). For the threo- and erythro-structures, appreciable frequency variations were found for the vibrations lying in the region 900-700 cm.$^{-1}$, namely ν_{19} and ν_{20}. In order to refine the frequency calculation, the A frequencies of poly(propylene-1, $1d_2$) were also calculated and the deviations of the calculated frequencies from those observed (ν_{19} and ν_{20})§ were used for correcting the corresponding frequencies as calculated for the threo- and erythro-structures. Thus the calculated frequencies, ν_{19} and ν_{20}, of poly(propylene-$1d_1$) were adjusted by +1.9% and −1.3%, respectively. The normal frequencies (900-600 cm.$^{-1}$) and potential energy distributions (a useful measure of the nature of normal vibrations) calculated for the threo- and erythro-structures are shown in Table I.

*The helical structures of the threo and erythro forms have been given in ref. 3, Figure 4.

†In the region 1300-600 cm.$^{-1}$, perpendicular bands of isotactic polypropylene are much weaker than parallel bands.

§The frequencies and potential energy distributions (%) are, ν_{19} (764 cm.$^{-1}$): CD_2 twist. (40), $r_{CC}{}^e$ (25); ν_{20} (691 cm.$^{-1}$): CD_2 rocking (70).

TABLE I

Frequencies ($cm.^{-1}$) and Potential Energy Distributions (%)
Calculated for the threo- and erythro-Diisotactic Poly(propylene-$1d_1$)

		ν	Potential energy distribution[a]
erythro	ν_{18}	886	CH_3 rock. (40), CD bend. (25)
	ν_{19}	786	CHD twist. (40), r_{CC}^{e} (30)
	ν_{20}	743	CHD rock. (80)
threo	ν_{18}	894	CH_3 rock. (30), CD bend. (35)
	ν_{19}	834	CHD twist. (25), r_{CC}^{e} (20)
	ν_{20}	722	CHD rock. (75)

[a] r_{CC}^{e}: Stretching mode of equatorial C–C bonds (6).

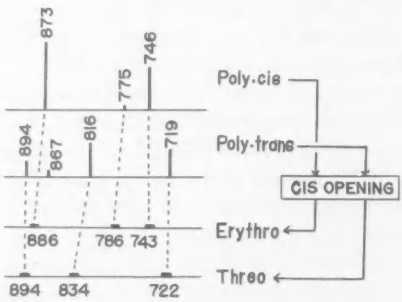

Fig. 1. The frequencies ($cm.^{-1}$) and relative intensities of the parallel bands of poly(propylene-$1d_1$-cis) and poly(propylene-$1d_1$-trans) (4) and the A frequencies calculated for the threo- and erythro-structures.

In Figure 1, the frequencies and relative intensities of the parallel bands of Poly-cis and Poly-trans (4) are compared with the frequencies calculated for the threo- and erythro-structures. From the correspondence between the observed and calculated frequencies, it may readily be concluded that poly(propylene-$1d_1$-cis) and poly(propylene-$1d_1$-trans) assume the erythro- and threo-diisotactic structures, respectively. Thus the polymerization of propylene with Ziegler-Natta catalysts is now found to occur by the cis-opening of the double bond. It is interesting to note that the polymerization of ethylene with Ziegler catalysts has also been found to occur by the cis-opening as revealed by the normal vibration analyses of poly(ethylene-$1,2d_2$) (8).

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THE CREEP OF POLYMETHYL METHACRYLATE IN THE β-REGION

There is a large discrepancy in the literature between the activation energy for creep, ΔH_c, in the β-region of polymethyl methacrylate (PMMA) and the activation energy obtained from internal friction, ΔH_{if}. The creep value was obtained by a variant of the superposition analysis and gave $\Delta H_c = 30$ kcal./mole (1), which was in good agreement with first determination of $\Delta H_{if} = 29$ kcal./mole (2). This value was not supported by two later determinations, $\Delta H_{if} = 18$ kcal./mole (3,4). If the latter value is accepted there is clearly a considerable discrepancy between ΔH_{if} and ΔH_c. The discrepancy is displeasing for several reasons one of which is the implication that there might be differences between the basic processes in internal friction and creep, a proposition which is opposed to the tenets of anelastic theory.

However, in the pioneer work of Kê (5) almost exact agreement was observed between ΔH_c and ΔH_{if} for the grain boundary relaxation in aluminium. This success we take to be due to the fact that the author normalized the creep curves before superposing them by dividing the creep strain at time t by the instantaneous strain at time zero. The effect of normalization is to remove from the derived ΔH_c any effect due to the temperature dependence of the limiting compliances. The latter statement assumes that the relaxed and unrelaxed compliances possess the same temperature coefficients. If this hypothesis is accepted for the β-relaxation in PMMA then it may be tested by measuring ΔH_c by superposing normalized creep curves and comparing the results with the value $\Delta H_{if} = 18$ kcal./mole.

Measurements of the creep compliance of PMMA were obtained at temperatures between -30 and $40°C$. The measurements were made in shear using apparatus similar to that of Morrison, Zapas, and De Witt (6). At each temperature T the creep compliances $J^T(t)$ were calculated making allowance for changes in the dimensions of the specimen due to thermal expansion. The compliances were found at all temperatures to be independent of applied stress at the strains used ($\epsilon_{max} \sim 10^{-3}$).

The normalization of $J^T(t)$ is carried out by calculating the unrelaxed compliance J_u^T with the help of a hypothesis: "the temperature dependence of Young's modulus measured at 10^5 cycles/sec. between -40 and $30°C$. (7) is due to temperature induced changes in the unrelaxed modulus." Then if $E^T(10^5)$ and $E^{T_0}(10^5)$ be the experimental values of Young's modulus at temperatures T and T_0 at 10^5 cycles/sec.

$$[E^{T_0}(10^5)/E^T(10^5)] = (J_u^T/J_u^{T_0}) = b_T \qquad (1)$$

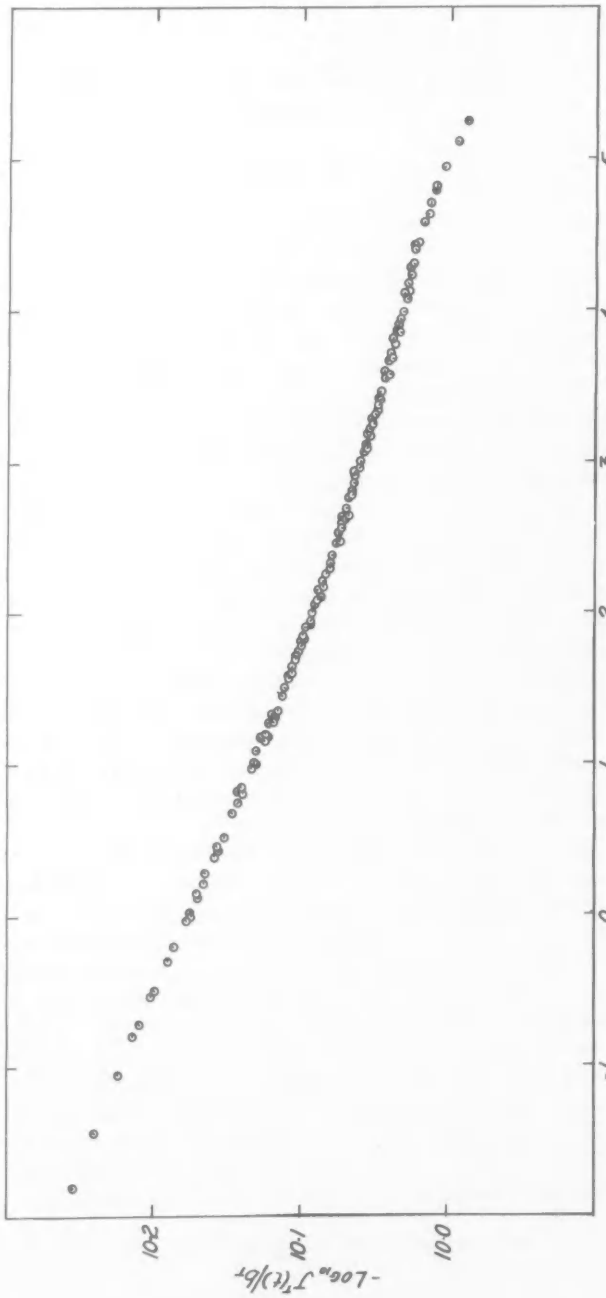

Fig. 1. The normalized creep curves superposed by horizontal shifts with respect to the creep curve at 1°C.: ◉ – 28.5°C.; ◉ – 11.5°C.; ◉ 1.0°C.; ◉ 10.0°C.; ◉ 19.2°C.; ◉ 32.0°C.; ◉ 40.8°C.

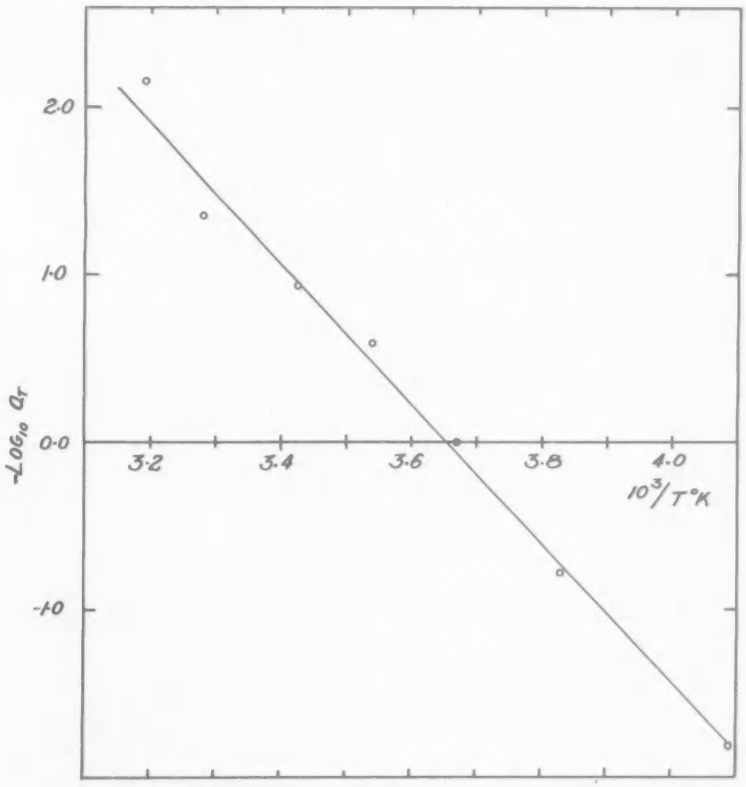

Fig. 2. The logarithm of the shift factor vs. $10^3/T°K$. Activation energy according to eq. 2, ΔH_c = 19 kcal./mole

taking Poisson's Ratio to be independent of temperature. Clearly a normalization analogous to that of $K\hat{e}$ is achieved by plotting the creep curves, $\log_{10}[J^T(t)/b_T]$ versus $\log_{10}t$.

The normalized creep curves are superposed by horizontal shifts along the $\log_{10}t$ axis, see Figure 1. The shift factors $\log_{10}a_T$ are plotted against $10^3/T$ in Figure 2. Assuming

$$\log_{10}a_T = (\Delta H_c/2.30R)\,[(1/T) - (1/T_0)] \qquad (2)$$

we find ΔH_c = 19 kcal./mole. This value is in good agreement with ΔH_{1f} = 18 kcal./mole.

By neglecting the normalization factor b_T and superposing the $\log_{10}J^T(t)$ versus $\log_{10}t$ curves we find ΔH_c = 34 kcal./mole. It is

therefore clear that agreement between ΔH_c and ΔH_{1f} is only obtained if the creep curves are normalized before superposition. This result supports the conclusions of an analogous experiment on the low temperature relaxation in polytetrafluoroethylene (8).

The hypothesis described by eq. 1 is of course an approximation to the truth. It can be argued that the agreement between ΔH_c and ΔH_{1f} shows it to be sufficiently true to be useful for the present purpose. There is other evidence in its favor which will be described elsewhere together with a complete description of the experiments.

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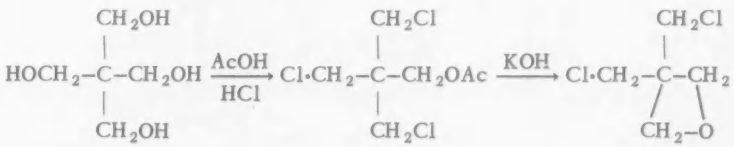
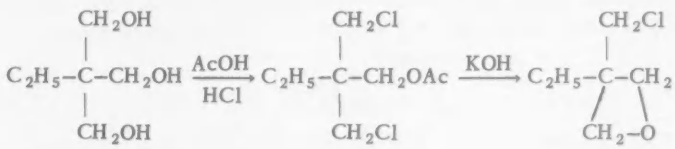
RADIATION INDUCED SOLID STATE COPOLYMERIZATION OF OXETANES

3,3-Bis(chloromethyl)oxetane was found to polymerize under gamma-irradiation very easily in the solid state (1-5). The following four oxetanes were synthesized (6) and copolymerized with each other as mixed crystals by gamma-irradiation.

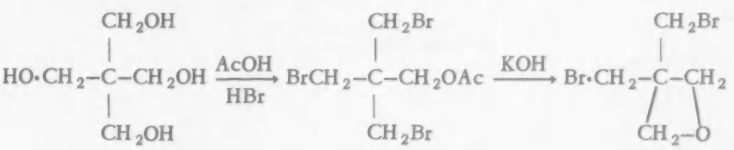
1. 3,3-Bis(chloromethyl)oxetane [BCMO] (7), m.p. 19°C.



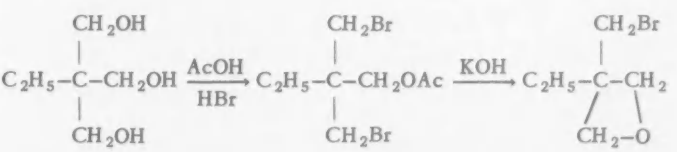
2. 3-Ethyl,3-chloromethyloxetane [ECMO], m.p. –3°C.



3. 3,3-Bis(bromomethyl)oxetane [BBMO] (7), m.p. 23.5°C.



4. 3-Ethyl,3-bromomethyloxetane [EBMO], m.p. 4°C.



Melting point measurement, differential thermal analysis, and x-ray diffraction analysis were examined both in monomer mixtures and in copolymers for the following four combinations: System I, BCMO–BBMO;

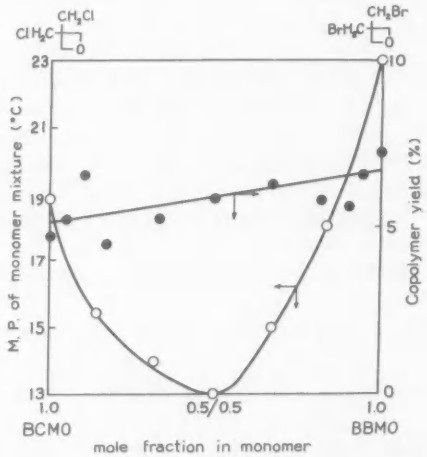


Fig. 1. Melting point of monomer mixture and polymer yield of radiation induced copolymerization in solid phase as a function of monomer composition. Dose rate = 3×10^4 r./hr.; polymerization time = 20.3 hr.; polymerization temperature = 0°C.; for 0°C. shock cooled crystal.

TABLE I

X-ray Diffraction Analysis of Monomer Mixture and Copolymer.

BCMO	BBMO	Monomer mixture BCMO–BBMO (Mole Ratio 0.5/0.5)
	Monomer Bragg angle (2θ)	
I. 17°57′(vw)	I. 21°12′(m)	I. 21°36′(s)
II. 21°12′(m)	II. 23°59′(m)	II. 25°32′(m)
III. 25°50′(m)	III. 26°53′(vw)	III. 27°23′(vw)
IV. 27°28′(vw)	IV. 28°54′(vw)	IV. 29°02′(w)
V. 29°02′(w)		
Poly-BCMO	**Poly-BBMO**	**Copolymer from BCMO–BBMO (Mole Ratio 0.5/0.5)**
	Polymer Bragg angle (2θ)	
I. 15°35′(s)	I. 20°51′(s)	I. 14°28′(w)
II. 21°12′(m)	II. 23°16′(w)	II. 21°21′(s)
III. 25°30′(w)	III. 27°42′(w)	III. 29°04′(vw)
IV. 29°23′(vw)	IV. 31°21′(w)	IV. 31°15′(w)

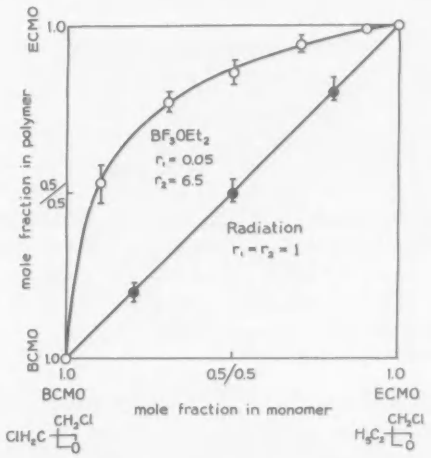


Fig. 2. Copolymer composition curves for radiation induced copolymerization of oxetanes A. (●) Radiation induced copolymerization in solid; (O) BF_3OEt_2 catalyzed copolymerization in liquid.

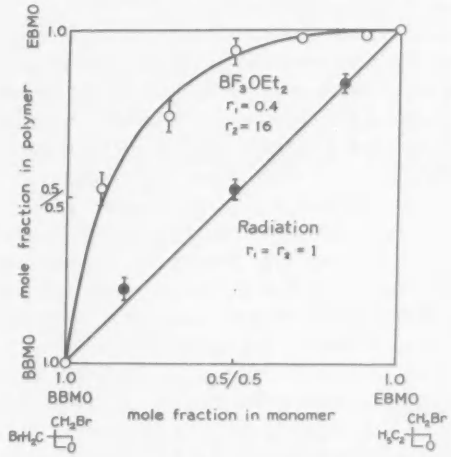


Fig. 3. Copolymer composition curves for radiation induced copolymerization of oxetanes B. Symbols the same as in Fig. 2.

System II, BCMO–ECMO; System III, ECMO–EBMO; System IV, BBMO–EBMO.

Figure 1 shows the melting points of monomer mixtures and the yield of copolymerizations against the monomer fractions in System I. The other three combinations were studied under similar conditions. Mixed

TABLE II

Monomer Reactivity Ratios

System	By BF_3-etherate (0.07 mole/liter at 30°C. for 0.5 hr.; [M] = 2 mole/liter in CH_2Cl_2)	By radiation in mixed crystals
I	$r_1 = 1$ $r_2 = 1$	$r_1 = 1$ $r_2 = 1$
III	$r_1 = 0.7$ $r_2 = 1.6$	$r_1 = 1$ $r_2 = 1$
II	$r_1 = 0.05$ $r_2 = 6.5$	$r_1 = 1$ $r_2 = 1$
IV	$r_1 = 0.4$ $r_2 = 16$	$r_1 = 1$ $r_2 = 1$

crystals obtained by shock cooling of System I were irradiated by gamma-rays at 0°C. for 20.3 hr. in the dose rate of 3×10^4 r./hr. Irradiated crystals were washed with methanol to remove the monomer remaining. The conversions of copolymerization were obtained in a rather poor reproducibility because of the slight change of crystallization conditions and because of the fact that a small amount of post polymerization is included (2,3,6).

In results on differential thermal analysis of copolymers and mixtures of homopolymers, the peak observed in the pattern of copolymers does not coincide for any peak observed in the mixtures of homopolymers. Also, x-ray diagrams of the mixed crystals of monomer mixtures are completely different from those of each monomer as represented by Bragg's angle (2θ) in Table I. This result shows the existance of a solid solution which was also confirmed by a phase diagram study. Table I also indicates the differences between copolymer and the mixture of homopolymers. It may be of interest to know the copolymer compositions obtained in the solid state copolymerization of these solid solution (8). Thus, the composition curves between copolymer and comonomer were obtained for systems II and IV, and compared with those catalysed by BF_3-etherate. The experimental results are shown in Figures 2 and 3. Reactivities of each monomer to the cationic polymerization are almost the same in System I, but largely different in Systems II, III, and IV as shown in the figures. Experimental results on the monomer reactivity ratios are summarized in Table II.

Table II shows that solid state copolymerization in mixed crystal makes a completely random copolymer according to the composition of monomer instead of its different reactivity. In the solid state the physical condition seems to predominate over the chemical reactivity for determining the composition of copolymer.

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POLYMER NEWS

SEMINAR ON STATISTICAL THEORY OF MACROMOLECULES

An intensive two-week seminar on topics in the Statistical Theory of Macromolecules will be conducted at Dartmouth College from August 19 through August 30 by Walter H. Stockmayer, Professor of Chemistry at Dartmouth, and Marshall Fixman, Professor of Chemistry and Director of the Institute of Theoretical Science at the University of Oregon. Places are still available at the session, which is sponsored by the National Science Foundation under its Advanced Science Seminar program.

Purpose of the seminar is to improve working knowledge of the statistical mechanics of macromolecular systems. Principal topics of the lectures, discussions and problem work include statistics of polymer structure and conformation, interactions between macromolecules, and dynamics of macromolecules. Some familiarity with the basic aspects of polymer science and of statistical mechanics will be assumed of participants.

Academic scientists are eligible for NSF stipends covering all tuition and living charges, plus a travel allowance. The inclusive fee for industrial scientists is $600. Applicants should write at once to Waldo Chamberlin, Dean of Summer Programs, Dartmouth College, Box 833, Hanover, N. H. Further information may also be had by telephoning Professor Stockmayer, Area Code 603, 643-3000, Ext. 501.

RHEO-OPTICS SYMPOSIUM

The Polymer Research Institute at the University of Massachusetts in Amherst, Massachusetts, will sponsor a one-day symposium on the "Rheo-optics of Polymers" on Saturday, August 24, 1963. This is the Saturday before the beginning of the International Rheology Congress at Brown University, Providence, Rhode Island, August 26–30. It is our hope that the proximity of this meeting in space and time will attract scientists from both this country and abroad. The Division of High Polymer Physics of the American Physical Society has been invited to cosponsor this symposium.

Dynamic-optical techniques for studying deformation and flow of polymers have been used to an increasing extent at the General Electric Laboratories, M.I.T., National Physical Laboratories (England), Hercules

Research Center, Bell Telephone Laboratories, Esso and several others. An initial conference here about 1-1/2 years ago indicated initial progress in the field of dynamic birefringence. Since then, in addition to extensive work in this field, studies have been undertaken in dynamic infrared dichroism, x-ray diffraction and light scattering. This general area of study has been christened "Rheo-optics" by Dr. Donald LeGrand.

The program will consist of about 12 invited papers. Housing and meals can be arranged in Amherst. If there is sufficient interest, sightseeing in New England and transportation to Providence could be arranged for Sunday, August 25.

For further information please write Prof. Richard S. Stein, Polymer Research Institute, University of Massachusetts, Amherst, Massachusetts.

Manuscripts should be submitted to one of the members of the Editorial Board or to the Editorial Office, c/o H. Mark, Polytechnic Institute of Brooklyn, 333 Jay Street, Brooklyn 1, New York. Address all other correspondence to Interscience Publishers, a Division of John Wiley & Sons, Inc., 605 Third Avenue, New York 16, New York.